Crossover Analyses of Heat Capacity and Susceptibility Measurements near the ^{3}He Liquid-Gas Critical Point

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An experiment called MISTE (Microgravity Scaling Theory Experiment) is being developed for a future mission on the International Space Station. The main objective of this flight experiment is to perform in-situ PVT, heat capacity at constant volume, C_V, and isothermal susceptibility, χ_T, measurements in the asymptotic region of the ^{3}He liquid-gas critical point. On the ground, gravity induces a density gradient that does not permit an accurate test of theoretical predictions within the asymptotic region. In preparation for this flight experiment, precision ground-based measurements are now being performed in the crossover region away from the critical point to determine the crossover parameters. Recent C_V and χ_T measurements along the critical isochore have been analyzed using a new crossover parametric equation-of-state and a field theoretical Renormalization Group calculation based upon the ϕ^4 model. A description of the experimental techniques and preliminary results of the theoretical analyses will be presented.

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1. INTRODUCTION

The introduction of the homogeneous postulate to explain the singular behavior of thermodynamic quantities near a critical point led to a set of scaling relations between the critical exponents that describe the expected leading and confluent power law singularities.[?] The application of Renormalization-Group theory[?] to the study of critical phenomena has provided a fundamental justification for the scaling relations. This RG theory has been used to calculate the critical exponents and universal asymptotic amplitude ratios for a wide range of universality classes. The most recent calculated values for these exponents[?] are believed to be highly accurate, and a majority of the scientific community is confident that these predictions correctly describe the asymptotic behavior of these systems. However, the situation is less well understood regarding the asymptotic amplitude ratios and the behavior in the crossover region where critical fluctuations no longer dominate the behavior of the system.

In the early years, emphasis was placed on theoretical and experimental studies of the liquid-gas critical point (which belongs to the 3-dimensional Ising model universality class) because this system permitted the measurement of a wide variety of thermodynamic properties within the critical region and could be used to test scaled equation-of-state models. In this system, the order parameter is the difference between the system's density and the critical density. Unfortunately, the liquid-gas critical point is subject to limitations resulting from the effects of gravity. In the Earth's gravitational field, a density stratification is induced in a fluid layer of finite vertical height. This stratification does not permit an accurate test of theoretical predictions within the asymptotic region. For this reason, a NASA flight experiment called "Microgravity Scaling Theory Experiment" (MISTE) was proposed to perform a set of thermodynamic measurements very close to the liquid-gas critical point of ^{3}He in a microgravity environment.[?]

The MISTE flight experiment plans to perform heat capacity at constant volume, C_V, isothermal susceptibility, χ_T, and PVT measurements in the same experimental cell. The objective is to obtain gravity-free measurements at least two decades in reduced temperature closer to the transition than can be obtained on the ground. The microgravity experiments should permit an accurate determination of the leading nonuniversal asymptotic critical amplitudes that will provide a more accurate analysis of crossover measurements farther away from the transition.

An exact determination of the asymptotic region cannot be made theoretically because the leading critical amplitudes are system dependent, and there are additional correction-to-scaling confluent singularities that also contain system-dependent amplitudes. Taking into account these correction-to-scaling terms leads to the following theoretical expressions for the heat capacity, C_V, and isothermal susceptibility, χ_T, along the critical isochore:

$$C_V^{\pm^*} = (T_c \rho_c / P_c) C_V^{\pm} = A_0^{\pm} |t|^{-\alpha} [1 + A_1^{\pm} |t|^{\Delta_s} + \ldots] + B_{\rm cr} \qquad (1)$$

$$\chi_T^{\pm^*} = (P_c / \rho_c^2) \chi_T^{\pm} = \Gamma_0^{\pm} |t|^{-\gamma} [1 + \Gamma_1^{\pm} |t|^{\Delta_s} + \ldots], \qquad (2)$$

where $\alpha \simeq 0.11$ and $\gamma \simeq 1.24$ are universal critical exponents and $A_0^\pm$ and $\Gamma_0^\pm$ are system-dependent critical amplitudes. The superscripts "+" and "–" correspond to positive and negative reduced temperatures $t \equiv (T - T_c)/T_c$, respectively. The system-dependent critical parameters are T_c, ρ_c, and P_c, and B_{cr} is a constant, fluctuation-induced term. The confluent singularity expansion in the brackets includes a new independent universal correction-to-scaling exponent,[?] $\Delta_s = 0.52 \pm 0.02$ and new system-dependent amplitudes $A_1^\pm$ and $\Gamma_1^\pm$. In analyzing heat-capacity measurements, an analytic background term B_a must be included. In the present analysis, we conveniently define this background term as a polynomial:

$$B_a = C_1 + C_2 t + C_3 t^2 + C_4 t^3. \tag{3}$$

2. RECENT GROUND-BASED MEASUREMENTS

Ground-based measurements along the critical isochore are now being performed in preparation for the MISTE flight experiment.[?] These measurements were performed in a flat pancake fluid cell shown in Fig. ??. A $GdCl_3$ high resolution thermometer (HRT) with a sensitivity of 1 nK at T_c = 3.31 K was used to measure the cell temperature. A parallel plate capacitor situated half way between the top and bottom of the cell served as a density sensor. The density was determined from the capacitance using the Clausius-Mossotti equation. A Straty-Adams type pressure sensor was also situated at the midplane of the cell. This sensor consisted of a parallel plate capacitor with one plate attached to a flexible diaphragm that sensed pressure changes in the cell. This configuration has the advantage that the heat capacity and susceptibility could be measured in the same cell and pressure, density and temperature data could also be continuously obtained.

The isothermal susceptibility, $\chi_T = \rho(\partial\rho/\partial P)_T$, was measured along isotherms in the single-phase region. This was achieved by initially overfilling the cell. Fluid was then slowly removed from the cell using an in-situ charcoal adsorption pump while maintaining a constant cell temperature. Susceptibility data were obtained from the $P - \rho$ curves in the reduced temperature range of $5 \times 10^{-4} < t < 10^{-1}$. The critical density was obtained from the inflection point in a $P - \rho$ curve that is associated with the inverse of the maximum of the susceptibility. As $t \to 0+$ the maximum of χ_T versus ρ approaches the critical density, ρ_c. The raw data can be smoothed and used to determine the density corresponding to the maximum in χ_T. After the susceptibility measurements, the low temperature valve was closed at the critical density. Then heat-capacity measurements were performed

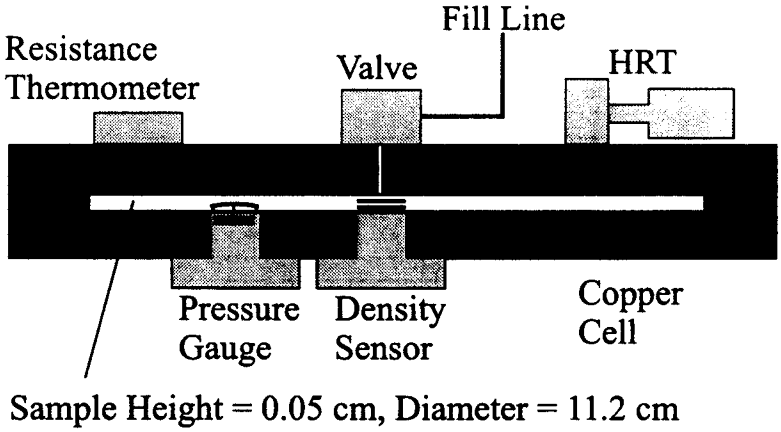

Fig. 1. Schematic of ground-based cell for measuring heat capacity and susceptibility.

using a pulse technique in the single and two phase regions over the range $5 \times 10^{-4} < |t| < 10^{-1}$. These new C_V and χ_T data agreed with earlier measurements from Horst Meyer's group[?,?,?] over the same temperature range. In the present analyses, we have used the recent data since they were obtained in the same cell during the same low temperature run.

3. CROSSOVER PARAMETRIC EQUATION OF STATE

The recent experimental data have been described using a new parametric crossover equation-of-state.[?] This equation-of-state is based on the original asymptotic extended parametric model that has been designed to satisfy all theoretically known asymptotic amplitude ratios.[?] The parametric representation of the scaling fields h_1, h_2, and the critical part $\Delta\tilde{P}$ of the dimensionless density of the thermodynamic potential, in terms of the parametric variables r and θ, is

$$h_1 = l_0 r^{\beta\delta}\theta(1-\theta^2), \tag{4}$$

$$h_2 = r(1-b^2\theta^2), \tag{5}$$

and

$$\Delta\tilde{P} = r^{2-\alpha}w(\theta) + \frac{1}{2}B_{\rm cr}r^2(1-b^2\theta^2)^2, \tag{6}$$

where $w(\theta)$ is an analytic function of θ

$$w(\theta) = m_0 l_0 \left[w_0 + w_1\theta^2 + w_2\theta^4 + w_3\theta^6\right]. \tag{7}$$

m_0 and l_0 are two system-dependent coefficients, and the term $\frac{1}{2}B_{\rm cr}r^2(1-b^2\theta^2)^2$ represents a fluctuation-induced caloric background. The order parameter is given by $\varphi_1 = (\partial\Delta\tilde{P}/\partial h_1)_{h_2}$. For simple fluids, to a first approximation $\varphi_1 = (\rho/\rho_c - 1)$, $h_2 = t$, and $h_1 = \mu - \mu_c$, which is the difference between the chemical potential μ and its critical value μ_c. The parameter b^2 and the coefficients w_0 ... w_3 are selected such that all asymptotic universal amplitudes ratios are satisfied within their theoretical accuracy with use of the approach suggested by Fisher et al.[?]

To develop a crossover parametric equation for the free energy, the variable r is rescaled in such a way that it provides the mean-field limit (van der Waals-like behavior) far away from the critical point. The equations for the scaling fields and the thermodynamic potential are also modified. The field h_1 is rescaled in the following way

$$h_1 = \tilde{l}_0 r^{3/2} Y^{(2\beta\delta-3)/2\Delta_s}\theta(1-\theta^2) \tag{8}$$

while the dependence of the field h_2 on r and θ is left unchanged. The crossover critical part $\Delta\tilde{P}_\times$ of the field-dependent thermodynamic potential $\tilde{P}(h_1, h_2)$ written in terms of r and θ becomes

$$\Delta\tilde{P}_\times(r,\theta) = r^2 Y^{-\alpha/\Delta_s}\tilde{w}(\theta) + \frac{1}{2}B_{\rm cr}r^2(1-b^2\theta^2)^2, \tag{9}$$

where

$$\tilde{w}(\theta) = \tilde{m}_0\tilde{l}_0\left[w_0 + w_1\theta^2 + w_2\theta^4 + w_3\theta^6\right], \tag{10}$$

$B_{\rm cr} = -2\tilde{m}_0\tilde{l}_0 w_0 < 0$ is a constant, $\tilde{m}_0 = m_0 g^{\beta-1/2}$, $\tilde{l}_0 = l_0 g^{\beta\delta-3/2}$, and $g = (\bar{u}\Lambda)^2/c_t$. In all, there are four system-dependent parameters. The parameters l_0 and m_0 determine two asymptotic critical amplitudes, while two crossover parameters $\bar{u}$ and $\Lambda/c_t^{1/2}$ determine the shape of crossover and the crossover temperature scale.[?] The parameter $\bar{u}$ is a normalized coupling constant, Λ is a dimensionless cutoff wavenumber, and c_t characterizes the range of intermolecular interaction. The form of the crossover function Y is the same as in the crossover Landau model developed on the basis of Renormalization-Group matching-point method:[?,?]

$$1-(1-\bar{u})Y = \bar{u}\left[1+(\Lambda/\kappa)^2\right]^{1/2} Y^{\nu/\Delta_s}, \tag{11}$$

with $\kappa^2 = c_t r Y^{(2\nu-1)/\Delta_s}$. In the asymptotic critical limit $Y \to (r/g)^{\Delta_s}$ so that

$$\Delta\tilde{P}_\times(r,\theta) \to \Delta\tilde{P}(r,\theta). \tag{12}$$

Far away from the critical point (as $r \to \infty$) $Y \to 1$ and the mean-field (classical) limit is recovered. It is important to emphasize that the universal

Table 1. Crossover parameters for ^{3}He obtained from the heat capacity and susceptibility data using the equation of state (EOS) and ϕ^4 models.

EOS joint fit Fig. ??		ϕ^4 fit Fig. ?? (Solid lines)	
$T_c^{\rm fit}$	3.315581	$T_c^{\rm fit}$	3.315533
$\bar{u}$	0.168	u/u^*	0.271 ± 0.015
$\Lambda/c_t^{1/2}$(fixed)	3.14	t_0 (fixed)	1.0
C_1	3.60 ± 0.08	C_1	2.95
C_2	16.9 ± 0.3	C_2	8.94
C_3	-233 ± 4	C_3	-55.7
C_4	-1140 ± 74	–	–
A_0^+	3.590 ± 0.001	A_0^+	4.00
Γ_0^+	0.150 ± 0.003	Γ_0^+	0.149 ± 0.001
A_1^+	0.712	A_1^+	0.84
Γ_1^+	0.941	Γ_1^+	1.000 ± 0.028

ratios of the first correction-to-scaling amplitudes are also satisfied by this equation-of-state within their theoretical accuracy.[?,?] The expressions for the correction-to-scaling amplitudes, which determine the start of crossover, are

$$\Gamma_1^+ = 0.590 g^{-\Delta_s}(1-\bar{u}), \tag{13}$$

$$A_1^+ = 0.446 g^{-\Delta_s}(1-\bar{u}). \tag{14}$$

The critical temperature determined from a previous experimental analysis in the ^{3}He system[?] is $T_c = 3.315533$ K. A joint fit of the heat-capacity and susceptibility data was performed with adjustable parameters $T_c^{\rm fit}$, $\bar{u}$, l_0, m_0, and the heat-capacity background parameters C_1 ... C_4. The heat-capacity data were analyzed above and below the critical point. The susceptibility data were fit in the range $t > 5 \times 10^{-4}$. Since the parameters $\bar{u}$ and $\Lambda/c_t^{1/2}$ are strongly correlated, we fixed the parameter $\Lambda/c_t^{1/2}$ at the value of $\Lambda/c_t^{1/2} = \pi$ (the value expected for the 3-dimensional Ising lattice with short range of interaction with $c_t = 1$).[?,?] The parameters l_0 and m_0 are related to the amplitudes of the heat capacity as $A_0^+ = 1.682 m_0 l_0$ and of the susceptibility as $\Gamma_0^+ = 3.383 m_0/l_0$. Thus, in a joint fit of the heat-capacity and susceptibility data the parameters l_0 and m_0 can be obtained. The analytic expressions for the leading and correction-to-scaling amplitudes are obtained by expanding the crossover function Y in powers of r^{Δ_s} near the critical point. The crossover parametric model yields the following leading universal amplitude ratios: $A_0^+/A_0^- = 0.524$ and $\Gamma_0^+/\Gamma_0^- = 4.94$. The results

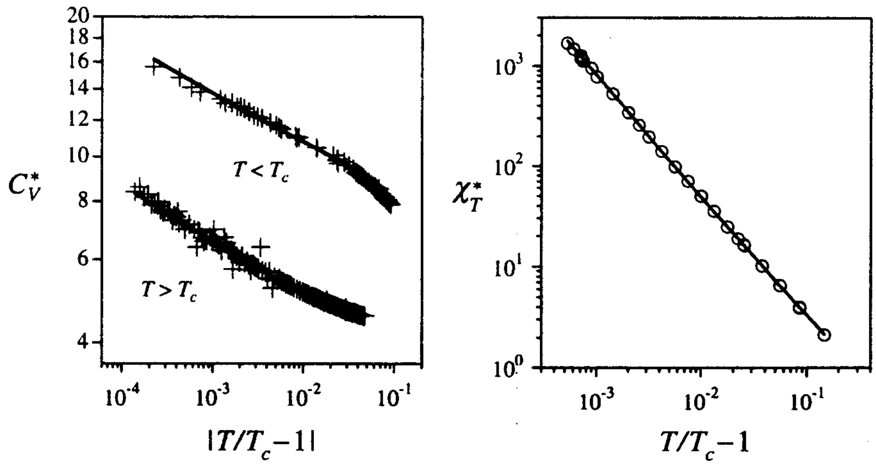

Fig. 2. Joint fit of critical isochore (zero-field) heat-capacity and susceptibility data for ^{3}He analyzed with the crossover parametric model.

of the fit for the heat capacity and susceptibility are shown in Fig. ?? and the resultant fit parameters and statistical errors are given in Table ??. In Fig. ?? we show deviations between the experimental data and the theoretical description for the joint fits of heat-capacity and susceptibility data.

4. RENORMALIZATION GROUP ϕ^4 MODEL

The heat-capacity and susceptibility measurements were also analyzed using a field theoretical Renormalization-Group (RG) ϕ^4 model[?] recently adapted to the $O(1)$ universality class.[?] This model, which is based on first principles, describes crossover behavior in terms of the RG flow parameter l. For this model, χ_T and C_V are given by

$$\chi_T^* = \chi_0 \, l^{-\gamma/\nu} \exp[-F_\varphi(l)] \,/\, f_\pm(u(l)) \tag{15}$$

$$C_V^* = C_0 \, l^{-\alpha/\nu} \exp[2F_r(l)] \; [\gamma^{-2}(l) + F_\pm(u(l))] \tag{16}$$

with the reduced temperature given by

$$t/b_\pm = t_0 \, l^{1/\nu} \exp[-F_r(l)] \; . \tag{17}$$

The functions F_φ, F_r, $f_\pm$ and $F_\pm$ were evaluated from Borel resummation of high-order perturbation series and $b_\pm$ are calculated at the fixed point

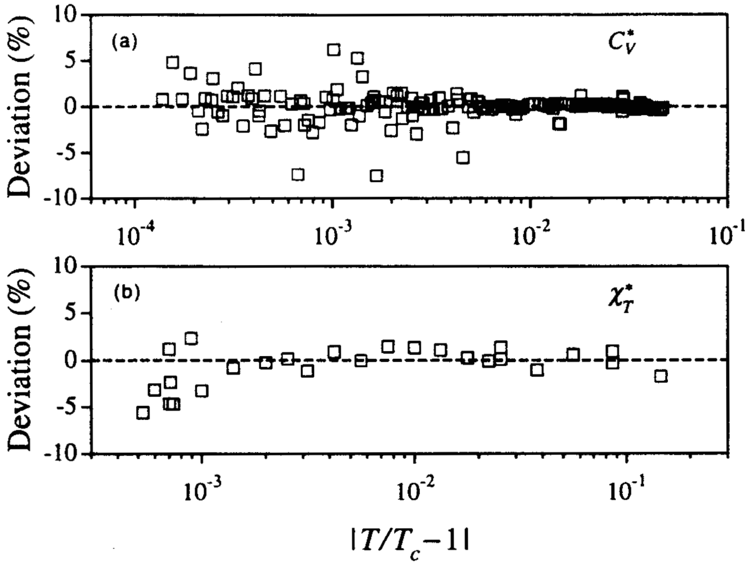

Fig. 3. Relative deviations (in percent) from a joint fit to the critical isochore (zero-field) heat capacity (a) and susceptibility (b) for ^{3}He using the crossover parametric model.

u^*.? The leading universal amplitude ratios predicted by this model are $A_0^+/A_0^- = 0.533$ and $\Gamma_0^+/\Gamma_0^- = 4.92$. There are five system-dependent parameters (t_0, u, χ_0, C_0 and γ^{-2}) associated with Eqs. (??) - (??). In the case of χ_T there are three non-universal parameters, χ_0, t_0, and the initial value of the coupling constant u. After eliminating the flow parameter l from the expressions, there remains only two independent parameters that we have chosen as u and χ_0 while setting $t_0 = 1$. The susceptibility data for $T > T_c$, previously fit? to the ϕ^4 model, using Eq. (??) yielded $u/u^* = 0.271$, $\chi_0 = 0.155$, $T_c^{\rm fit} = 3.315533$ K, and a correction-to-scaling amplitude $\Gamma_1^+ = 1.00$ that is consistent with the Γ_1^+ value obtained in Table ?? for the parametric equation-of-state analysis. The susceptibility data were fit first since background effects are much less important than in the case of the heat capacity.

The recently obtained heat-capacity data were fit both to the ϕ^4 model close in to the transition, using Eq. (??) and then to this model including analytical background terms. In this analysis there remains two model parameters, C_0 that is related to $A_0^{\pm}$, and γ^{-2} that accounts for $B_{\rm cr}$. The least square fits to the data were performed using u/u^* and T_c obtained from the previous susceptibility analysis.? The results of fitting the data over the

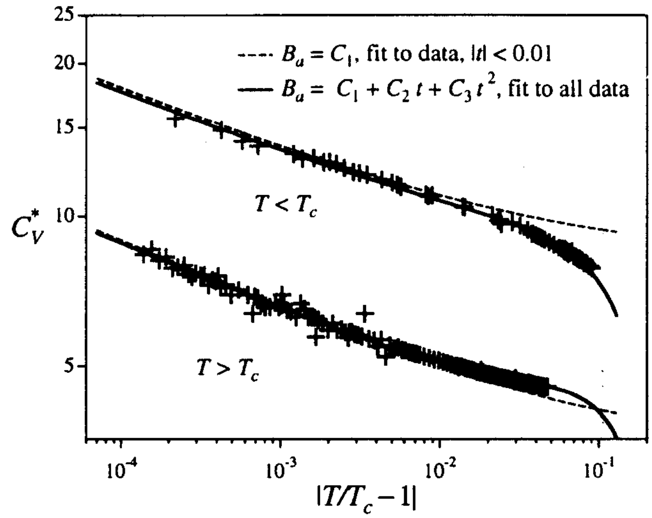

Fig. 4. Critical isochore heat-capacity data for ^{3}He analyzed with the ϕ^4 model.

reduced temperature range $|t| < 10^{-2}$ including only a constant analytic background term, C_1, is shown by the dashed lines in Fig. ??. The best fit parameter $C_0 = 0.380$. We see that the extrapolation of this fit to temperatures farther away from the transition is poor. The fit to all the data including temperature dependent background terms is shown by the solid lines in Fig. ?? with the best fit parameter $C_0 = 0.386$, which is close to the value obtained from the pure ϕ^4 model fit. The constant background terms B_{cr}, determined from γ^{-2}, and C_1 are strongly correlated and cannot be unambiguously determined from the fitting procedure. The ϕ^4 parameters for C_V and χ_T obtained from fitting all the data including statistical errors assuming a 2% measurement uncertainty are given in Table ??.

In summary, both the EOS and ϕ^4 initial fitting procedures show good agreement with experiment. However, a better understanding of the nature of the heat-capacity background farther away from the transition and the influence of possible quantum effects is crucial for a stringent test of these models. The influence of the background will be significantly reduced by performing heat-capacity measurements in microgravity. These measurements closer to the transition can be used to determine the leading critical amplitudes, $A_0^{\pm}$, and constant background that will then reduce the adjustable parameters required for testing crossover models.

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